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Development of Phosphorylated Adhesives

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SUMMARY

The synthesis of epoxy prepolymers containing phosphorus was carried out in such a manner as to provide adhesives containing at least 5 percent of this element. The purpose of this was to impart fire retardant properties to the adhesive. The two epoxy derivatives, bis(4-glycidyl-oxyphenyl)phenylphosphine oxide and bis(4-glycidyl-2-methoxyphenyl)phenylphosphonate, and a curing agent, bis(3-aminophenyl)methylphosphine oxide, were used in conjunction with one another and along with conventional epoxy resins and curing agents to bond Tedlar and Polyphenylethersulfone films to Kerimid-glass syntactic foam-filled honeycomb structures. Elevated temperatures ($>100^{\circ}\text{C}$) are required to cure the epoxy resins with the phosphorus-containing diamine; however, when Tedlar is being bonded, lower curing temperatures must be used to avoid shrinkage and the concomitant formation of surface defects. Thus, the phosphorus-containing aromatic amine curing agent cannot be used alone, although it is possible to use it in conjunction with an aliphatic amine which would allow lower cure temperatures to be used. The experimental epoxy resins have not provided adhesive bonds quite as strong as those provided by Epon 828 when compared in peel tests, but the differences are not very significant. It should be noted, however, that a more comprehensive formulation optimization effort is needed, if optimum properties are to be realized. In any case the fire retardant characteristics of the neat resin systems obtained are quite pronounced, since in most cases the self-extinguishing properties are evident almost instantly when specimens are removed from a flame.

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1. INTRODUCTION

Among the compounds commonly used in fire-retardant compositions are those containing phosphorus such as the phosphate esters, arsenic such as in arsenic thioarsonate and certain other additive type materials. Although the addition of such materials to polymers can be effective in reducing flammability, the fluid additives tend to migrate to the surface, where, in the case of thin films, they gradually evaporate from the film surface. This migration effect can also induce adhesive failure if the additive has migrated to the adhesive-substrate interface.

Problems such as these can be circumvented by incorporating phosphorus directly into the polymer molecular structure, where it will be bound as part of the adhesive macrostructure.

In addition, although phosphorus is expected to provide fire retardant characteristics to the adhesive, potential toxic by-products such as those encountered with brominated or arsenic-containing fire retardant materials should be significantly reduced.

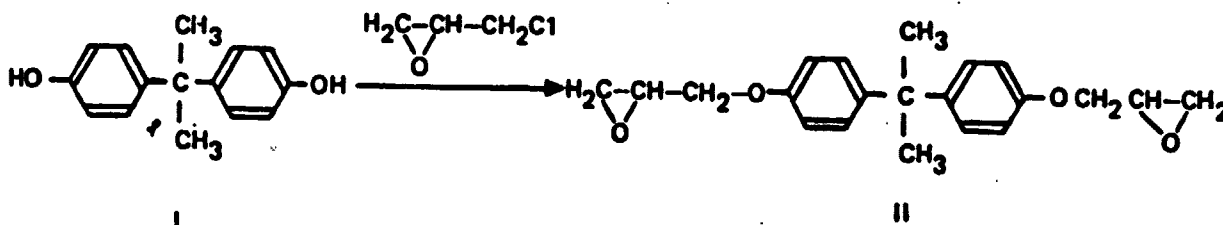
To accomplish the program objectives, two phosphorus-containing epoxy-type compounds analogous in structure to that of the diglycidyl ether of bisphenol A were prepared. In addition, a phosphorus-containing aromatic diamine was prepared to serve as a potential curing agent. Stoichiometric formulations of the experimental epoxy compounds with the phosphorus bearing diamine as well as with various aliphatic amine curing agents were prepared and used to bond both Tedlar and polyphenylether sulfone films onto polyimide (Kerimid) glass honeycomb structure. Details of the formulation effort are discussed later in this report. Furthermore, since some of these combinations were excessively brittle, some adhesives were compounded with small amounts of a conventional epoxy resin to introduce improved flexibility and toughness.

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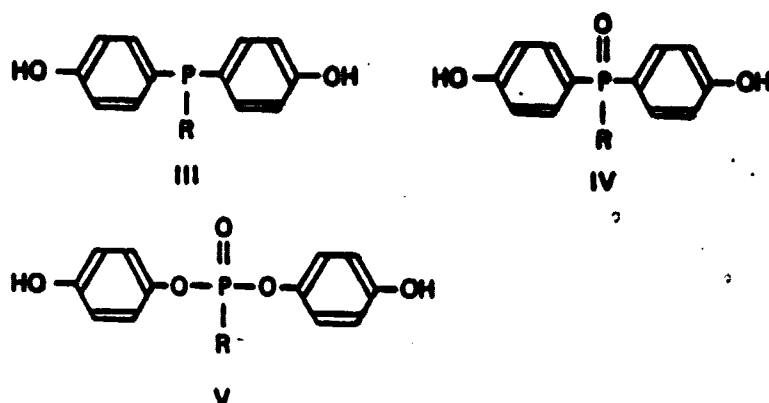
II. OLIGOMER SYNTHESIS

A. BACKGROUND AND DESCRIPTION

The direction of the synthetic approach initially was to prepare epoxy compounds which were structurally similar to that of the diglycidyl ether of bisphenol A(I), but which would incorporate phosphorus in the molecular structure so as to introduce fire-retardancy. As a first step in achieving these objectives phosphorus-bearing phenols had to be synthesized. These phenols could subsequently be reacted with epichlorohydrin to give the diglycidyl ether derivative in a manner similar to the preparation of the diglycidyl ether of bisphenol A shown below:

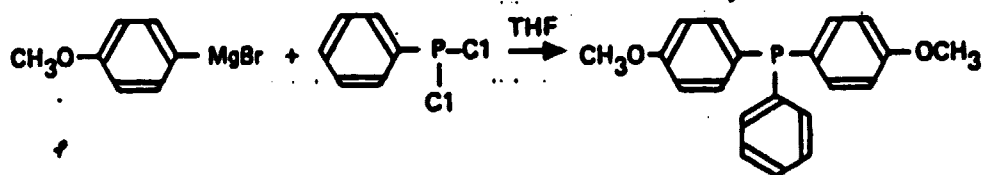


Because of the ready availability of starting materials, phosphines, phosphine oxides and phosphonate derivatives are suitable candidate reactants for this purpose. Thus, if one were to substitute for the isopropylidene group in I an appropriate phosphorus-containing moiety, one would obtain III, IV, or V, where R is a methyl or phenyl group. Since phosphine compounds are known to be toxic, compounds of type IV were preferred over that of type III.

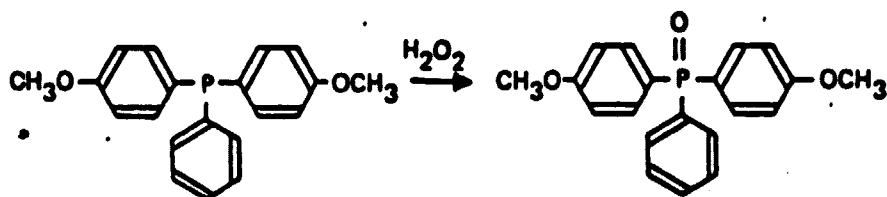


Also, in subsequent reactions of compounds of this class, phosphines are relatively reactive as they are strong nucleophiles, while the phosphine oxide moiety is quite unreactive.

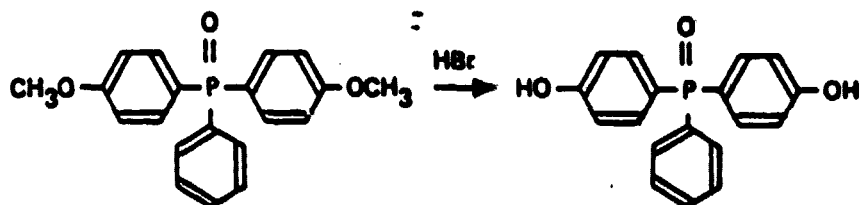
In this sequence of reactions, p-bromoanisole was converted to its Grignard reagent in tetrahydrofuran and subsequently reacted with dichlorophenylphosphine to give bis(4-methoxyphenyl)phenylphosphine, a solid, in 70 percent yield. This reaction is illustrated below:



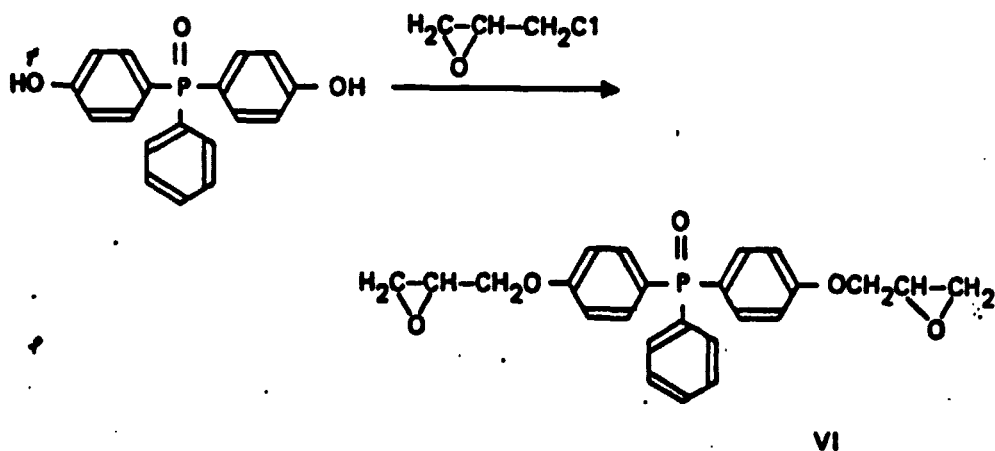
This phosphine was oxidized in the presence of dilute aqueous hydrogen peroxide to give bis(4-methoxyphenyl)phenylphosphine oxide, a difficultly crystallizable solid, in 90 percent yield. The phosphine oxide was then



demethylated in 48 percent aqueous hydrobromic acid solution to give an 80 percent yield of bis(4-hydroxyphenyl)phenylphosphine oxide, a high melting solid. This phosphorylated bisphenol derivative was then reacted with



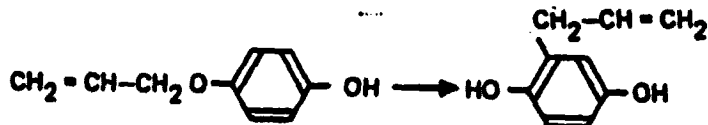
excess epichlorohydrin in basic solution to give bis(4-glycidyloxyphenyl)-phenylphosphine oxide (VI) as a viscous liquid product containing 7.4 percent phosphorus.



The synthesis of the alternate class of compounds, the phosphonates, was to have involved the reaction of hydroquinone with either dichlorophenylphosphine or phenylphosphonic dichloride. Initial attempts on this approach with dichlorophenylphosphine were negative. With variations in the mole ratios of reactants and solvent concentrations, results of the reactions in tetrahydrofuran and pyridine showed only small amounts of intractable materials. In parallel reactions carried out in aqueous sodium hydroxide solution buffered with sodium hydrogen phosphate, no insoluble product was observed after neutralization with hydrochloric acid. The poor results

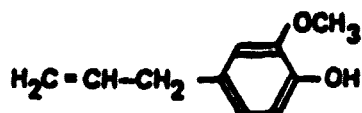
obtained in the reactions carried out in THF indicated that an appropriate substitute choice for hydroquinone might afford a useful product. Thus, both resorcinol and bisphenol A were used in an attempt to promote solubility differences which would facilitate the separation of products from the starting materials. In both cases, either a very low yield of product was obtained or the product was intractable.

These results appeared to suggest that difunctional molecules such as hydroquinone and resorcinol have a much greater tendency to polymerize than to form the monomeric compounds required to prepare the prepolymers described previously. Thus, it was suggested that a phenolic substance with a vinyl-containing substituent which can be epoxidized could be used to avoid the problem of premature polymerization. Ideally, p-allyloxyphenol would have suited this purpose but it readily rearranges to a substituted hydroquinone derivative and therefore would not be a useful intermediate. The rearrangement proceeds as shown below.

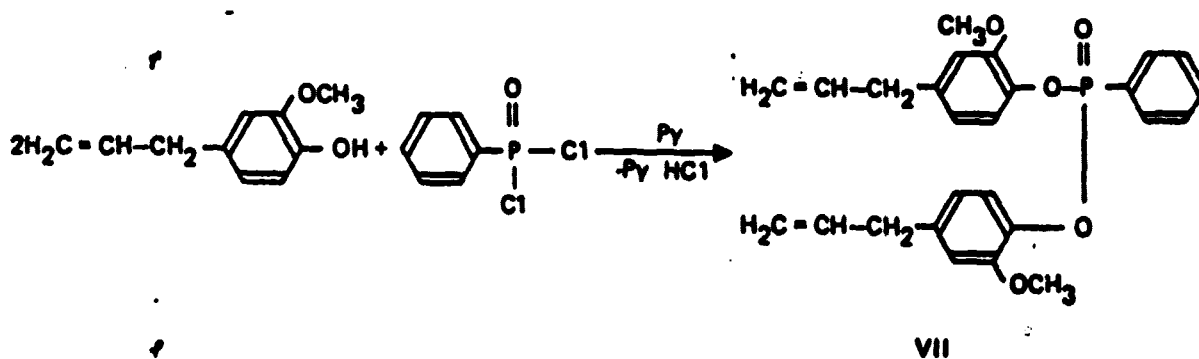


An analogous candidate was p-allylphenol, which differs from p-allyloxyphenol in that the allyl group is one atom nearer the ring, but would not be expected to alter its reactivity significantly. However, the synthesis of this compound is difficult in that it must be separated from its isomers. The availability of a naturally occurring substance, eugenol (4-allyl-2-methoxyphenol), whose methoxy group does not interfere with the reactivity of the allyl group, was selected as the reactant for phosphonate formation. The effect of the methoxy substituent is not only to reduce the acidity of the phenolic hydrogen when compared to phenol, but to increase the hydrolytic

stability of the phosphonate ester it forms by sterically hindering the hydrolysis reactions which can take place. The structure of this material is as follows:

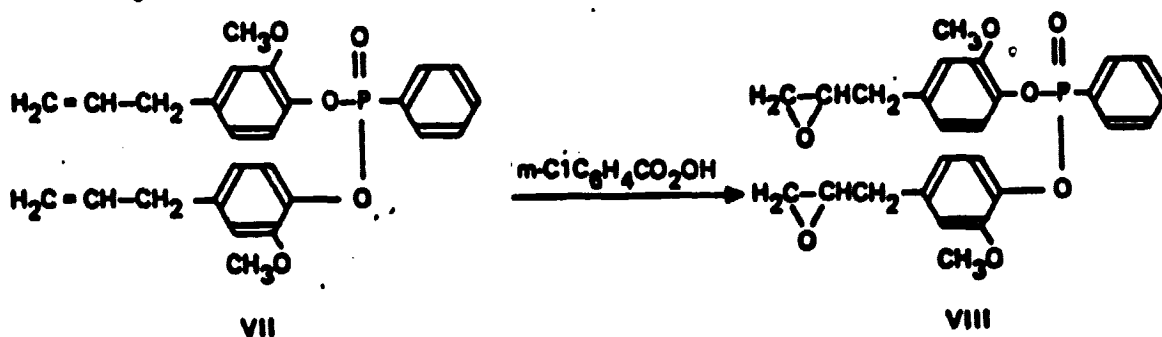


Phenylphosphonic dichloride was reacted with 4-allyl-2-methoxyphenol in pyridine to give bis(4-allyl-2-methoxyphenyl) phenylphosphonate (VII), a viscous liquid, which gave a major fraction boiling at ca 90°C at 28 microns pressure when distilled by molecular distillation. The synthesis was carried out as follows:



Heating to 120°C at this pressure resulted in decomposition and/or polymerization of the product. Since non-drastring conditions appeared essential for the purification of the phosphonate ester, the work-up procedure for the reaction mixture utilized an ether-water extraction process. The significance of the procedure was indicated when the infrared spectral properties of the product of the extraction and that obtained by molecular distillation were identical in every respect. A more complete purification was carried out by the technique of column chromatography, where the phosphonate was eluted with chloroform on activity No. 3 alumina. The IR and NMR spectra of the product were consistent with the proposed structure.

The phosphonate ester was then treated with m-chloroperoxybenzoic acid to give bis(4-glycidyl-2-methoxyphenyl) phenylphosphonate (VIII) as shown in the following equation:

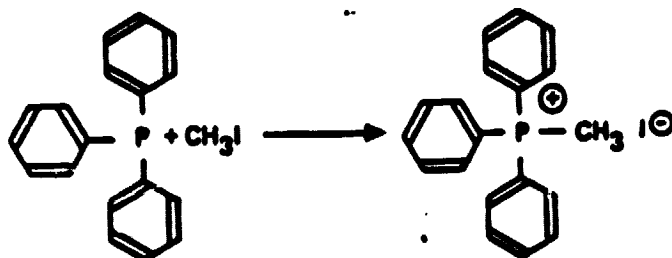


The infrared spectrum of this product showed the disappearance of olefinic absorption but the appearance of hydroxyl and carbonyl absorption. The reaction has been carried out in chloroform, both at room temperature and at reflux. In each case the infrared spectrum was similar, but epoxide absorption was obscured by the phosphonate group. Since the chloroform solution of the reaction mixture was sensitive to the aqueous work-up procedure in that large volumes of water resulted in poor phase separation, some epoxide ring opening may have occurred in the presence of the by-product m-chlorobenzoic acid. Because the product was quite viscous and extremely high boiling, it was purified by chromatography on a column of neutral alumina, activity No. 3, with ethanol as the eluent. The product obtained by this technique showed no hydroxyl or carbonyl absorption in the infrared spectrum and gave an NMR spectrum consistent with the proposed structure. The epoxy equivalent obtained prior to chromatographic separation was 303, while that obtained subsequently was 277. This compares reasonably well to the theoretical value of 242.

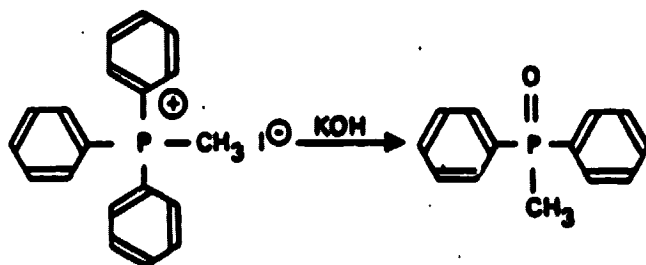
B. CURING AGENT SYNTHESIS

The approach to the preparation of a phosphorus-containing curing agent is described in the steps leading to the synthesis of bis(m-aminophenyl)-methylphosphine oxide.

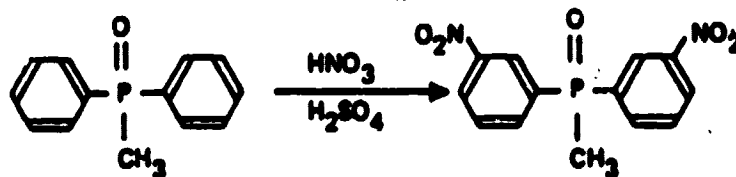
Triphenylphosphine was reacted with methyl iodide in an ether-chloroform solution to give a quantitative yield of methyltriphenyl phosphonium iodide.



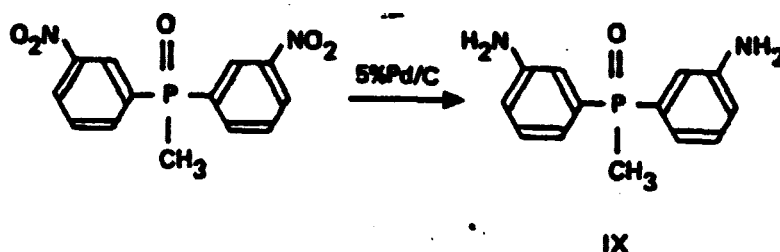
This in turn was treated with aqueous potassium hydroxide solution to give methyldiphenylphosphine oxide in 80% yield. The oxide was then nitrated



to give bis(m-nitrophenyl)methylphosphine oxide, a yellow solid, in 75 percent yield.



The literature shows very few references to the reduction of nitro-substituted aromatic phosphine oxides. Although there was no indication of problems with the phosphine oxide moiety, it appeared to be important that no unreacted phosphine derivative be present since the common hydrogenation catalysts may be poisoned. The nitro compound was reduced with 5 percent palladium on carbon in ethanol solvent. The reaction proceeded rapidly and cleanly to give bis(3-aminophenyl)methylphosphine oxide (IX), a solid with a melting range of 152-155°C, in 85 percent yield. This reaction is shown below:



III. SCREENING STUDIES

Preliminary screening studies were carried out with bis-(4-glycidyloxyphenyl)phenylphosphine oxide (VI) and a common curing agent such as HV, a mixture of menthanediamine, m-phenylenediamine, and benzyldimethylamine. The curing agent bis(m-aminophenyl)methylphosphine oxide (IX) was compared in compatibility with VI and Epon 825 as a standard epoxy resin. The results in Table I show that the mixture of VI with a standard HV mixture of curing agents easily cured at elevated temperatures. Room temperature reaction only caused gel formation even after 24 hours, but on exposure to elevated temperatures brittle solids were obtained. When epoxy resin VI was reacted with the phosphorus-containing amine IX, curing again occurred at elevated temperatures to give brittle solids, except where the quantity of curing agent was less than the stoichiometric equivalent of the epoxy resin. Similarly, room temperature cures caused only gel formation. When a standard epoxy such as Epon 825 was cured with the phosphorus-containing amine IX, only gel formation was observed at room temperature. However, at elevated temperatures, the epoxy resin and the phosphorylated amine separated as distinct phases and, due to this incompatibility, no curing took place. However, it was subsequently shown that homogeneous cured resins could be made if an amine-terminated prepolymer was first synthesized in acetone and subsequently freed of solvent. The incompatibility is not observed when both curing agent and resin are phosphorylated species. Experimental epoxy resin bis(4-glycidyl-2-methoxyphenyl) phenylphosphonate (VIII) cured easily with either HV or curing agent IX but both compositions give brittle solids. All cured samples showed self-extinguishing properties when removed from a flame. Only a small amount of soot and no smoke was observed during the burning of any sample.

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TABLE I. RESULTS OF PRELIMINARY CURING STUDIES
ON PHOSPHORYLATED EPOXY COMPOUNDS

Epoxy Compound, A	Curing Agent, B	Weight Ratio A/B	Temperature (°F)	Time (Hr.)	Result
VI	HV	10/1.5	68	16	gel
VI	HV	10/2.0	68	16	gel
VI	HV	10/1.5	160	16	brittle solid
VI	HV	10/2.0	160	16	brittle solid
VI	HV	10/2.0	230	8	brittle solid
VI	IX	10/2.0	68	16	gel
VI	IX	10/4.0	68	16	gel
VI	IX	10/1.0	160	72	gel
VI	IX	10/1.5	160	72	brittle solid
VI	IX	10/2.0	160	25	brittle solid
VI [*]	IX	10/4.0	160	16	brittle solid
Epon 825	IX	10/2.0	68	16	gel
Epon 825	IX	10/4.0	68	16	gel
Epon 825	IX	10/2.0	160	16	phase separation
Epon 825	IX	10/4.0	160	16	phase separation
Epon 825	IX	10/1.5	160	72	phase separation
Epon 825 [*]	IX	10/1.0	160	72	phase separation
VIII	HV	10/2.0	110	8	brittle solid
VIII	IX	10/2.0	110	8	brittle solid

IV. ADHESIVE BONDING STUDIES

Initial studies of the bond strengths of adhesives formulated with bis-(4-glycidyl-2-methoxyphenyl) phenylphosphonate (VIII) and bis(4-glycidyl-oxyphenyl)phenylphosphine oxide (VI) were made by comparing the experimental adhesive formulations with a cured mixture of Epon 828 and Epon 732, using T-peel specimens prepared in the following manner:

A one-inch by three-inch aluminum panel etched for ten minutes at 150°F under standard conditions was bonded to a pre-washed epoxy-glass sheet with an epoxy-polyamide resin system (B. F. Goodrich A-1177-B) at 125°F overnight. This provided a firm support for the epoxy-glass substrate. A sample of Tedlar film, whose surface was prepared by etching it with a solution of sodium in tetrahydrofuran-naphthalene, was then pressed onto the epoxy-glass substrate, which had been coated with the epoxy resin-curing agent mixture. Curing proceeded for 16 hours at 250°F. The results of the peel strength tests carried out at a 90° angle to the substrate surface are shown in Table II.

The peel strengths shown here are relatively low, but this is attributed primarily to an inadequate etching process carried out at Hughes on the untreated Tedlar film initially used in this work. Adhesive studies were continued on polyimide (Kerimid)-glass syntactic form filled composite honeycomb panels using Tedlar film and Polyphenylethersulfone film. All three of these materials were provided to Hughes by NASA-Ames Research Center. For the purpose of this study, the Kerimid honeycomb composite was cut into 3" x 1/2" x 1" specimens, which were scrubbed with Ajax along with the films described above. The experimental epoxies were first used neat, with diethylaminopropylamine as the curing agent, and then were compounded with

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TABLE II. PEEL STRENGTHS OF DIETHYLAMINOPROPYLAMINE
CURED EPOXY BONDED TEDLAR/EPOXY-GLASS

Epoxy Resin		Wt. Ratio A/A'/B*	Ave. Peel Strength (lbs)
A	A'		
Epon 828	Epon 732	50/50/6	0.22
VIII	—	100/0/6	0.20
VIII	Epon 732	75/25/6	0.13
VI	—	100/0/6	0.04
VI	Epon 732	75/25/6	0.0
*Diethylaminopropylamine			

Hysol R2119 to reduce the somewhat brittle character of the cured resins. The results of the peel tests carried out at 90° angle to the substrate surface are shown in Table III. The values obtained with the materials provided by NASA were much improved over those obtained previously and shown in Table II. Except for compound VIII compounded with Hysol R2119, the results indicate slightly better adhesion to Polyphenylethersulfone film than to Tedlar film, although both films showed peel strengths of approximately 1.2 lbs/in of width. However, it must be noted that the film thickness of the former (5 mils) is much greater than that of the latter (1 mil). With Polyphenylethersulfone film, the average peel strengths were greatest when the experimental epoxies were used neat, rather than when compounded with Hysol R2119. In both Tables II and III, the compounding of the experimental epoxies with standard flexibilizing resins generally reduces the peel strength relative to the neat resin.

The adhesive bond strength of the experimental epoxies to the Kerimid honeycomb substrates also were compared using m-phenylenediamine and the experimental diamine, bis(m-aminophenyl)methylphosphine oxide (IX), as the curing agents. The results of these studies are shown in Table IV.

**TABLE III. PEEL STRENGTHS OF ADHESIVES FORMED FROM
BLENDS OF EXPERIMENTAL RESINS, HYSOL R2119 AND
DIETHYLAMINOPROPYLAMINE USING TEDLAR AND
POLYPHENYLETHERSULFONE FILMS BONDED
TO KERIMID/GLASS LAMINATES****

Epoxy Resin		Cure Conditions	Wt. Ratio A/A'/B*	Ave. Peel Strength (lbs/inch of width)	
A	A'			Tedlar	Polyphenyl- ethersulfone
VIII	Hysol R2119	160°F, 8 hrs	80/20/6	1.17	0.37
VIII	—	160°F, 8 hrs	100/0/6	0.26	0.83
VI	Hysol R2119	160°F, 8 hrs	80/20/6	0.04	0.94
VI	—	160°F, 8 hrs	100/0/6	0.11	1.25

*Diethylaminopropylamine
**Kerimid-glass honeycomb structure provided by NASA-Ames Research Center.

**TABLE IV. PEEL STRENGTHS OF ADHESIVES FORMULATED
FROM EXPERIMENTAL EPOXY RESINS CURED WITH
m-PHENYLENEDIAMINE AND BIS(m-AMINOPHENYL)-
METHYLPHOSPHINE OXIDE**

Epoxy Compound	Curing Agent	Cure Conditions	Wt. Ratio A/B	Ave. Peel Strength (lbs/inch of width)	
				Tedlar***	Polyphenyl- ethersulfone
VI	mpd*	240°F, 6 hrs.	10.5/1.0	0.70	0.20
VI	IX	240°F, 6 hrs.	4.6/1.0	0.60	0.30
VIII	mpd*	240°F, 6 hrs.	10.0/1.0	**	0.65
VIII	IX	240°F, 6 hrs.	4.5/1.0	0.75	<0.1

*m-phenylenediamine
**Film broke before testing
***Film shrinkage occurs at the cure temperature!

Except for the adhesive formed from VIII and IX, the Polyphenylethersulfone film results presented in Table IV were somewhat comparable to those shown in Table III. However, at this cure temperature, there was a noticeable shrinkage in the Tedlar film resulting in a wrinkled appearance of the film surface. Outgassing also was observed and the adhesive formulations were quite thixotropic. Although the Polyphenylethersulfone film was virtually unaffected at this elevated temperature, a lower cure temperature was obviously needed for bonding Tedlar film. Since aromatic amines are not generally effective at a lower temperature it was deemed essential to use aliphatic amine curing agents for the Tedlar film. Thus, in subsequent experiments the epoxy compounds VI and VIII were cured with aminoethyl-piperazine (AEP) and diethylenetriamine (DET). These formulations, cured at only 125°F, provided smooth Tedlar film surfaces after cure. The results of these tests are compared in Table V to those obtained with Epon 828. Peel strengths were, however, not as good as the best values shown in Table III, and it is evident that additional formulation studies are needed if bond strengths are to be optimized.

Visual inspection of the adhesives listed in Table V showed them to be transparent. In addition, all test specimens had smooth surfaces. The results also show that under the same test conditions the samples prepared with Epon 828 are somewhat better than those obtained with experimental resins V and VIII. Furthermore, the variation in values observed in previous tables are more likely a result of substrate and film preparation techniques than they are due to significant changes resulting from the use of different curing agents. It is expected that the optimization of the substrate preparation parameters along with those of the curing temperatures, incorporating blends where the reduction of fire retardant capability was minimal, would provide acceptable adhesive bonding characteristics between the substrate and the difficultly bonded films.

It must be concluded, therefore, that additional formulation and optimization work, as well as film etching studies are needed. It should be noted, however, that Tedlar film is available with several finishes, and only one type has been tested in this study.

TABLE V. COMPARISON OF THE PEEL STRENGTHS OF ADHESIVES
FORMED FROM EPOXY COMPOUNDS VI AND VIII,
DIETHYLENETRIAMINE (DET) AND AMINOETHYLPIPERAZINE (AEP)

Epoxy Compound	Curing Agent	Cure Conditions	Wt. Ratio A/B	Ave. Peel Strength (lbs/in. of width)	
				Tedlar	Polyphenyl- ethersulfone
VI	DET	125°F, 24 hrs.	13.8/1	0.20	0.14
VI	AEP	125°F, 24 hrs.	6.6/1	0.16	0.07
VIII	DET	125°F, 24 hrs.	13.5/1	0.13	0.09
VIII	AEP	125°F, 24 hrs.	6.4/1	0.11	0.05
Epon 828	DET	125°F, 24 hrs.	9.1/1	0.12	0.18
Epon 828	AEP	125°F, 24 hrs.	4.3/1	0.24	—

V. EXPERIMENTAL PROCEDURES

A. SYNTHESIS OF BIS(3-AMINOPHENYL)METHYLPHOSPHINE OXIDE

Into a 500 ml 3-neck flask were placed triphenylphosphine (39.3 g, 0.15 mole, Aldrich, 99 percent), chloroform (130 ml) and ether (200 ml). To this was added dropwise with stirring at room temperature excess methyl iodide (10 ml, Aldrich) during 30 min. Stirring was continued overnight. The white solid which had precipitated was filtered, washed with ether and dried under vacuum. The dried solid (63 g) was refluxed in a mixture of water (300 ml) and 40 percent aqueous KOH (75 ml) and the benzene evolved was collected. The reaction mixture was cooled to room temperature and washed with 3 x 100 ml and 2 x 50 ml of benzene, which were separated and dried over MgSO_4 . The solvent was evaporated under reduced pressure to give 82 percent yield of diphenylmethylphosphine oxide, a white solid, mp 110-113°C.

A solution of nitric acid in concentrated H_2SO_4 was prepared by adding 150 ml of conc H_2SO_4 to 150 ml of 90 percent nitric acid in an ice bath. This solution, after cooling to room temperature, was added to a solution of diphenylmethylphosphine oxide (52 g, 0.24 mole) in 98 percent H_2SO_4 (175 ml) at ice temperature during two hours, maintaining the temperature at $<10^\circ\text{C}$. The ice bath was removed and stirring was continued for two hours. The reaction mixture was slowly poured with stirring into 1500 ml of a mixture of water and ice to give a gummy yellow residuc, which, on continued stirring and dilution with water, slowly crystallized. The solid was washed with water until the aqueous washings were neutral to Congo Red indicator. Recrystallization from 2:1 ethanol-acetic acid (600 ml) afforded bis(3-nitrophenyl)-methylphosphine oxide, 75 percent yield of a yellow crystalline solid, mp 202-205°C.

Into a 500 ml Parr bottle were placed bis(3-nitrophenyl)methylphosphine oxide (31.6 g, 0.1 mole), 95 percent ethanol (200 ml) and 5 percent palladium on powdered charcoal (2.0 g, Sargent-Welch). The bottle was placed on the Parr hydrogenator at ambient temperature under 3 atmospheres of hydrogen pressure until hydrogen uptake ceased (ca. 2 hours). The mixture was filtered through Celite and the filtrate evaporated under reduced pressure to give an orange-brown viscous liquid residue, which, on addition of 200-300 ml of an equivolume hexane-benzene mixture, gave a 95 percent yield of bis(3-aminophenyl)methylphosphine oxide, a tan solid, mp. 152-155°C.

B. SYNTHESIS OF BIS(4-HYDROXYPHENYL)PHENYLPHOSPHINE OXIDE

A mixture of p-methoxyphenylmagnesium bromide (3.0 moles) and phenyldichlorophosphine (1.25 moles) in tetrahydrofuran (3000 ml) was refluxed 3 hours, poured over ice, and acidified with hydrochloric acid. After standing overnight to allow the THF to evaporate, the product was taken up in benzene, washed with water, and extracted with four 1000 ml portions of concentrated hydrochloric acid. The acid extracts were cautiously neutralized with concentrated ammonia, giving an oil which solidified on cooling. The solid was filtered, washed, dried, and recrystallized from 2000 ml of methanol, yielding 271 g (75 percent) of colorless crystals, mp 89-90°C.

To the bis(p-methoxyphenyl)phenylphosphine (6.44 g, 0.07 mole) prepared in this way in acetone (30 ml) distilled over KMnO_4 , was added dropwise at 0°C during 5 minutes, 10 ml of a solution of hydrogen peroxide prepared by mixing 10 ml of 30 percent hydrogen peroxide with 20 ml of water. The reaction mixture was stored for one hour and washed with 0.3M aqueous ferrous ammonium sulfate (30 ml). The solution was then washed with benzene (25 ml), which was washed with 2 x 25 ml of water, filtered, and dried over anhydrous Na_2SO_4 . The product was filtered and the solvent evaporated to give a viscous liquid residue, which, when diluted with benzene and hexane, gave 90 percent of bis(p-methoxyphenyl)phenylphosphine oxide, a white solid on standing, mp 96-98°C.

¹ Bride, Cummings, and Pickles, J. Appl. Chem. II, 352 (1961)

Into a 1000 ml flask was placed bis(p-methoxyphenyl)phenylphosphine oxide (58 g, 0.17 mole) and 48 percent hydrobromic acid (Baker) (300 ml). The solution was refluxed with a condenser attached to a trap to collect methyl bromide (5 hours). The reaction mixture was cooled to room temperature and the acidic solution was decanted. The gummy residue was dissolved in 600 ml of 1.5 M aqueous sodium hydroxide and neutralized with glacial acetic acid, giving a gummy solid which, on stirring in ice, gave a caked solid. The solid was filtered and dried and recrystallized from methanol (460 ml) to give 40 g of bis(4-hydroxyphenyl)phenylphosphine oxide, mp 235-239°C.

Into a 500 ml 3-neck flask equipped with a condensate collector and separation chamber designed to return excess epichlorohydrin (Aldrich) to the reaction flask, a mechanical stirrer, and a dropping funnel, were placed bis(4-hydroxyphenyl)phenylphosphine oxide (57 g, 0.184 mole) and excess epichlorohydrin (140 ml, 1.84 mole). The reservoir was filled with epichlorohydrin so that evolved water caused continuous addition of epichlorohydrin to the reaction mixture. The reaction mixture was heated to reflux, and to this was added dropwise during 3 hours a solution of 40 percent aqueous NaOH (36.74 g). The reaction mixture was diluted with benzene, filtered, and the filtrate evaporated under reduced pressure to give a cloudy yellow viscous liquid. The epoxide equivalent was 265 compared to the theoretical value of 211.

C. SYNTHESIS OF BIS(4-ALLYL-2-METHOXYPHENYL) PHENYLPHOSPHONATE

Into a flask equipped with a condenser, stirrer, and addition funnel was placed eugenol (66 g, 0.4 mole) and pyridine (100 ml). To the flask, cooled to 0°C, was added dropwise with stirring phenylphosphonic dichloride (41 g, a slight excess) during two hours. The solution was allowed to stir overnight at room temperature. The reaction mixture was cooled to 0°C and filtered to remove precipitated salts. The filtrate was diluted with water (50 ml) and the aqueous layer washed with 2 x 200 ml of ether. The

²Sencar, Valient, and Worth, J. Org Chem. 25, 2001, 1960.

ether solutions were combined with the organic phase, which was then washed with 2 x 250 ml of 5 percent aqueous H_2SO_4 solution, 250 ml of 5 percent aqueous $NaHCO_3$ solution, and distilled water until the aqueous washings were neutral to litmus paper. The ethereal solution was dried over Na_2SO_4 , filtered, and evaporated under reduced pressure to give a pale yellow liquid. Final purification was carried out by chromatographic separation on a wet neutral alumina column (activity no. 3) using $CHCl_3$ as solvent. Olefin-containing fractions were dried over sodium sulfate and solvent removed by rotary evaporation to give a pale yellow liquid, whose infrared and NMR spectra were consistent with the proposed structure.

D. SYNTHESIS OF BIS(4-GLYCIDYL-2-METHOXYPHENYL) PHENYLPHOSPHONATE

Into a flask were placed bis(4-allyl-2-methoxyphenyl) phenylphosphonate (38.0 g, 0.084 mole) and chloroform (40 ml). To this solution, cooled to ice temperature, was added dropwise with stirring during two hours a solution of m-chloroperoxybenzoic acid (40 g, 0.23 mole, excess) in chloroform (360 ml). Stirring was continued at ambient temperature overnight. The reaction mixture was cooled to $0^\circ C$ and filtered to remove the precipitated m-chlorobenzoic acid. The filtrate was washed with 100 ml of 20 percent aqueous $NaHSO_3$ solution, 3 x 60 ml of 10 percent aqueous $NaHCO_3$ solution, and 3 x 70 cc of saturated $NaCl$ solution. The phases were separated and the chloroform phase dried over Na_2SO_4 . The system was filtered and evaporated under reduced pressure to give approximately 30 g of dark red viscous liquid product, which was chromatographed on a wet neutral alumina column (activity no. 3) using ethanol as the eluent. Epoxide-containing fractions were combined and the solvent was removed by rotary evaporation to give a viscous yellow-brown liquid, whose infrared and NMR spectra were consistent with the proposed structure. The epoxide equivalent was 277 compared with the theoretical value of 242.

APPENDIX A
PRELIMINARY MATERIAL AND APPLICATION SPECIFICATION
for
PHOSPHORUS CONTAINING FIRE RETARDANT ADHESIVES

1.0 SCOPE

This specification covers the basic techniques for production and application, including the minimum performance requirements, for two fire retardant, low toxicity adhesive systems. Each system consists of a phosphorus-containing epoxy resin and an amine curing agent.

2.0 CLASSIFICATION

The fire retardant adhesive systems (epoxy resin and curing agent), covered by this specification shall be classified as follows:

- Type I - P2835 Adhesive - Suitable for bonding of polyphenylethersulfone film
- Type II - P2844 Adhesive - suitable for bonding of polyvinyl fluoride film (Tedlar)

3.0 APPLICABLE DOCUMENTS

3.1 The following documents form a part of this specification.

Federal

QQ-A-250/5 Aluminum Alloy, Alclad 2024 Plate and Sheet

American Society for Testing and Materials

- D445 Kinematic Viscosity of Transparent and Opaque Liquids
- D568 Flammability of Flexible Plastics
- D891 Specific Gravity of Industrial Hydrocarbons
- D1002 Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal), Test for
- D1544 Color of Transparent Liquids - Gardner Color Scale
- D1652 Epoxy Content of Epoxy Resins
- D1876 Peel Resistance of Adhesives (T-Peel Test)
- D2074 Total Primary, Secondary and Tertiary Amine Values of Fatty Amines by Alternative Indicator Method

D2117 Melting Point of Semicrystalline Polymers

D2393 Viscosity of Epoxy Compounds and Related Components,
Test for

3.2 Other Publications:

Scott's Standard Methods of Chemical Analysis, Vol. 1., 5th Ed., 1961,
D. Van Nostrand Co., Princeton, N. J.

4.0 REQUIREMENTS

4.1 Qualification

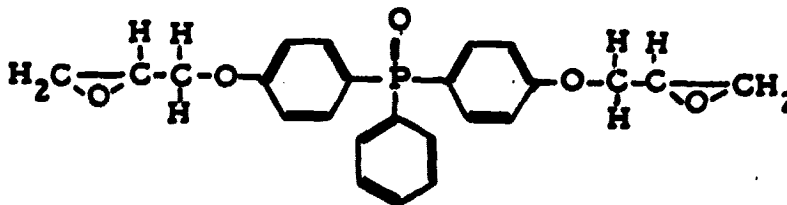
The adhesive furnished under this specification shall be a product which
has been tested and passed the qualification tests specified herein.

4.2 Material

4.2.1 Type I Adhesive System

The epoxy component for the Type I adhesive system shall consist of the
following:

bis(4-glycidyloxyphenyl)phenylphosphine oxide



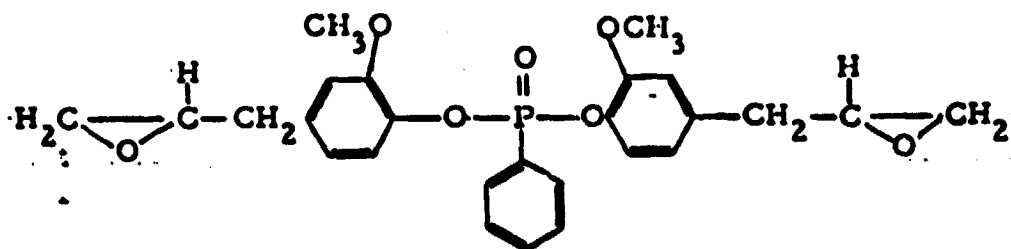
The curing agents used with this resin are

N, N-diethylaminopropylamine (DEAPA) and m-phenylenediamine. Both
are readily available commercially.

4.2.2 Type II Adhesive System

The phosphorus-containing epoxy component for the Type II system shall
consist of the following:

bis(4-glycidyl-2-methoxyphenyl) phenylphosphonate,



In addition to the above epoxy resin a diglycidyl ether epoxy, e. g., Hysol R2119 or equivalent, is blended with the phosphorus-containing resin in the ratio of 1 part diglycidyl ether to 4 parts of the phosphorus-containing epoxy compound. The curing agents for the above mixture are also N,N-diethylaminopropylamine (DEAPA) and m-phenylenediamine.

4.3 Preparation Techniques

4.3.1 Type I Epoxy Resin - bis (4-glycidyloxyphenyl)phenylphosphine oxide¹

A mixture of p-methoxyphenylmagnesium bromide (3.0 moles) and phenyl-dichlorophosphine (1.25 moles) in tetrahydrofuran (3 liters) is heated at reflux for 3 hours, poured over ice, and acidified with hydrochloric acid. After standing overnight to allow the THF to evaporate, the product is taken up in benzene, washed with water, and extracted with four 1-liter portions of concentrated hydrochloric acid. The acid extracts are cautiously neutralized with concentrated ammonia giving an oil which solidifies on cooling. The solid is filtered, washed, dried, and recrystallized from 2 liters of methanol, yielding 271 g (75%) of colorless crystals, mp 89-90°C.

To the bis(p-methoxyphenyl)phenylphosphine (6.44 g, 0.02 mole) in acetone (30 ml) distilled over KMnO_4 , is added dropwise at 0°C, during a 5 minute period, 10 ml of a solution of hydrogen peroxide prepared by mixing 10 ml of 30% hydrogen peroxide (Baker) with 20 ml of water. The reaction mixture is stirred for one hour and the organic layer is washed with 30 ml (0.3 mole) of aqueous ferrous ammonium sulfate. The solution is then washed with benzene (25 ml), which is washed with 2 x 25 ml of water, filtered and dried over anhydrous Na_2SO_4 . The product is filtered and the

(1) Senear, Valient, and Worth, J. Org. Chem. 25, 2001, 1960

solvent evaporated to give a viscous liquid residue, which, when diluted with benzene and hexane, gives 90% of bis(p-methoxyphenyl)phenylphosphine oxide, a white solid, mp 96 - 98°C.

Into a 1 liter flask is placed bis(p-methoxyphenyl)phenylphosphine oxide (58 g, 0.17 mole) and 48% aqueous hydrobromic acid (Baker) (300 ml). The solution is refluxed with a condenser attached to a trap to collect methyl bromide (5 hours). The reaction mixture is cooled to room temperature and the acidic solution is decanted. The gummy residue is dissolved in 600 ml of 1.5 Molar aqueous sodium hydroxide and neutralized with glacial acetic acid, giving a gummy solid which, on stirring in ice, gives a caked solid. The solid is collected by filtration and dried, then recrystallized from methanol (460 ml) to give 40 g of bis(4-hydroxyphenyl)phenylphosphine oxide, mp 235-239°C.

Into a 500 ml 3-neck flask equipped with a condensate collector, a separation chamber designed to return excess epichlorohydrin (Aldrich Chem. Co.) to the reaction flask, a mechanical stirrer and a dropping funnel are placed 57 g(0.184 mole) bis(4-hydroxyphenyl)phenylphosphine oxide and excess epichlorohydrin (140 ml, 1.84 mole). The reservoir is filled with epichlorohydrin so that evolved water will cause continuous addition of epichlorohydrin to the reaction mixture. The reaction mixture is heated to reflux, and to this mixture is added dropwise, during a 3 hour period, a solution of 40% aqueous NaOH (36.74 g). The reaction mixture is diluted with benzene, filtered, and the filtrate is evaporated under reduced pressure to give a cloudy yellow viscous liquid.

4.3.2 Type II Epoxy Resin - bis(4-glycidyl-2-methoxyphenyl) phenylphosphonate

Into a flask equipped with a condenser, stirrer, and addition funnel is placed eugenol (66g, 0.4 mole, Aldrich) and pyridine (100 ml). To the flask cooled to ice temperature is added dropwise with stirring phenylphosphonic dichloride (41g) over a two hour period. The solution is allowed to stir overnight at room temperature. The reaction mixture is cooled to 0°C and

filtered to remove precipitated salts. The filtrate is diluted with water (50 ml) and the aqueous layer washed with 2 x 200 ml of ether. The ether solution is combined with the organic phase, which is then washed with 2 x 250 ml of 5% aqueous H_2SO_4 solution, 250 ml of 5% aqueous NaHCO_3 solution, and distilled water until the aqueous washings are neutral to litmus paper. The ethereal solution is dried over Na_2SO_4 , filtered, and evaporated under reduced pressure to give a pale yellow liquid. Final purification is carried out by chromatographic separation on a wet neutral alumina column (activity #3) using CHCl_3 as the solvent. Olefin-containing fractions are dried over sodium sulfate and the solvent removed by rotary evaporation to give a pale yellow liquid, whose infrared and nmr spectrum is consistent with the structure of bis(4-allyl-2-methoxyphenyl) phenylphosphonate.

Into a flask is placed bis(4-allyl-2-methoxyphenyl) phenylphosphonate (38.0g, 0.084 mole) and chloroform (40 ml). To this solution, cooled to 0°C , is added dropwise with stirring during two hours a solution of m-chloroperoxybenzoic acid (40 g, 0.23 mol, excess) in chloroform (360 ml). Stirring is continued at ambient temperature overnight. The reaction mixture is cooled to 0°C and filtered to remove the precipitated m-chlorobenzoic acid. The filtrate is washed with 100 ml of 20% aqueous NaHSO_3 solution, 3 x 60 ml of 10% aqueous NaHCO_3 solution, and 3 x 70 cc of saturated NaCl solution. The phases are separated and the chloroform phase dried over Na_2SO_4 . The system is filtered and evaporated under reduced pressure to yield approximately 30 g of dark red viscous liquid product, which is chromatographed on a wet neutral alumina column (activity #3) using ethanol as eluent. Epoxide-containing fractions are combined and the solvent is removed by rotary evaporation to give a viscous yellow-brown liquid, whose infrared and NMR spectra are consistent with the proposed structure. The epoxide equivalent is 277, compared with the theoretical value of 242.

4.4 Properties

4.4.1 Phosphorus-Containing Epoxy Resins

Table I shows the properties of Type I and Type II epoxy resins containing phosphorus.

Table I. Epoxy Resin Properties

Property	Value	
	Type I	Type II
Epoxide equivalent weight	265 \pm 20	277
Viscosity, 25°C (relative to dichloromethane)	1.04	1.01
Color, Gardner maximum	5	12.5
Specific gravity, 25°/25°C	1.23 \pm 0.05	1.15 \pm 0.05
Phosphorus content, %, min.	7.5	6.4

4.4.2 Shelf Life

The cured adhesives shall be capable of conforming to the minimum shear strength requirements at 25 \pm 5°C (77 \pm 9°F) after storage of the individual components for six years at ambient conditions (10° to 35°C) in moisture proof sealed containers in the absence of sunlight.

4.4.3 Adhesive Physical Properties

The adhesive systems described by this specification, when formulated in the ratio of 6 parts of curing agent to 100 parts of epoxy or the 4:1 epoxy blend, and cured in accordance with the directions given below, shall meet the requirements shown below, and in Table II.

4.4.3.1 Working characteristics

4.4.3.1.1 Application (pot) life. The application life of a 150 gram batch of either adhesive, when mixed and ready for use at 75 \pm 10°F (24 \pm 6°C), shall be a minimum of one hour. The material shall be considered to have reached the end of its working life when the viscosity reaches 160,000 centipoises.

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4.4.3.1.2 Curing time and temperature. When maintained at a temperature of $160 \pm 5^{\circ}\text{F}$ ($71 \pm 3^{\circ}\text{C}$) ($344 \pm 3^{\circ}\text{K}$) at the bond line, both types of adhesives shall cure in 8 hours.

4.4.3.1.3 Curing pressure. The adhesives shall be capable of curing and making satisfactory bonded joints as described within this specification when only contact pressure is applied during the period of cure.

4.4.3.2 Mechanical properties. Bonded specimens shall conform to the mechanical requirements specified in Table II.

Table II. Mechanical Properties of Bonded Joints

Test	Test Condition	Substrates		Value	
		Type I	Type II	Type I	Type II
Lap Shear strength* Mega pascals, min (psi) min.	Room temp	Al - Al	Al - Al	950 [6.55]	1165 [8.03]
Peel Strength** Newtons/meter [lb/in of width] min.	Room temp	polyimide- glass to Poly- phenyl- ether- sulfone	polyimide- glass to Tedlar	219 [1.25]	205 [1.17]

4.4.3.3 Transparency. It shall be possible to easily read normal newsprint through a section of either type adhesive cast to a thickness of $1 \text{ mm} \pm 0.2 \text{ mm}$ ($0.040 \pm 0.008 \text{ in}$) thick.

4.4.3.4 Flammability. 0.125 mm ($.005 \text{ in.}$) thick polyphenylethersulfone film, and/or polyvinyl fluoride (Tedlar) film coated on one side with cured adhesive, $0.05\text{-}0.08 \text{ mm}$ thick ($0.002\text{-}0.003 \text{ in}$), shall be self-extinguishing in a maximum of 5 seconds, when tested in accordance with paragraph 5.3.6.10.

4.5 Workmanship

The workmanship shall be such as to ensure a product which is uniform and free of gel particles, dirt, moisture or other contaminants, and other defects that would affect the material's properties.

*Lap shear specimens made using m-phenylenediamine curing agent.

**Peel strength specimens made using DEAPA curing agent.

5.0 QUALITY ASSURANCE PROVISIONS

5.1 Responsibility for Inspection

Unless otherwise specified in the contract or the purchase order, the supplier is responsible for the performance of all the inspection requirements as specified herein. The supplier may utilize his own facility or any commercial laboratory acceptable to NASA-Ames Research Center. The processing activity, or its designated representative, reserves the right to perform any or all of the inspections set forth in the specification where such inspections are deemed necessary to ensure that supplies and services conform to prescribed requirements.

5.2 Classification of Examinations and Test

All of the examinations and testing of the adhesive systems shall be classified as qualification tests. Qualification tests shall be performed on samples submitted for approval as qualified products and shall be performed on individual lots of products submitted for acceptance. The qualification tests are listed in Table III. A certified test report from the supplier shall accompany each product submitted for approval and each lot of adhesive system submitted for acceptance.

5.3 Sampling

Samples for product qualification or for qualified lot acceptance shall be as specified in Paragraph 5.3.2. The material preparation shall conform to the requirements of Paragraph 4.2 herein. A test report from the supplier shall accompany each sample to be tested, and shall show the composition number and the test results for all requirements of this specification and shall refer specifically to the applicable paragraphs herein. All the adhesive system materials manufactured and formulated as one batch shall be considered a lot and shall be numbered as such for purposes of inspection.

5.3.1 Rejection and Retest

Failure of any lot to conform to all applicable requirements of this specification shall be cause for retest. Property or properties in question shall be retested on new specimens prepared from the same lot of adhesive system

coating. If the results of test of the second sample fails to meet the specification requirements, the entire lot shall be rejected.

5.3.2 Specimens

All samples to be tested shall be prepared in accordance with the applicable test method.

5.3.3 Size and Number of Specimens

The size and number of specimens for conformance to each requirement are listed in Table III.

5.3.4 Test Methods

Unless otherwise specified, the following conditions shall be used for testing.

- | | |
|----------------|---|
| a. Temperature | Room Ambient, $21^{\circ} - 27^{\circ}\text{C}$ ($70^{\circ} - 80^{\circ}\text{F}$) |
| b. Humidity | Facility ambient to 90% relative humidity |

In the event of conflict, referee tests shall be conducted at $23^{\circ} \pm 2^{\circ}\text{C}$ ($73.4^{\circ} \pm 3.6^{\circ}\text{F}$) and $50 \pm 10\%$ relative humidity.

5.3.5 Test Sequence

Unless otherwise specified herein, test sequence shall be optional.

5.3.6 Test Methods and Procedures

5.3.6.1 Epoxide equivalent

The epoxide equivalent weight shall be determined in accordance with ASTM D1652 for conformance to Table I.

5.3.6.2 Viscosity

The viscosity of the epoxy resin shall be determined in accordance with ASTM D445 using a Cannon - Fenske viscometer or equivalent, to establish conformance to Table I. The viscosity of a solution of 0.5 gm of epoxy resin in 100 ml of dichloromethane is compared to the viscosity of a pure dichloromethane sample.

5.3.6.3 Color

The colors of the epoxy resins shall be tested in accordance with ASTM D1544 to establish conformance to Table I. The supplier may certify the color values in lieu of conformance testing.

5.3.6.4 Specific gravity

The specific gravity of the epoxy resin shall be determined in accordance with ASTM D891 to establish conformance to Table I.

5.3.6.5 Phosphorus Content

The phosphorus content shall be determined in accordance with the procedure given in Scott's "Standard Methods of Chemical Analysis, Vol. 1, 5th Ed, p. 694, "Gravimetric Methods for Determination of Phosphorus."

5.3.6.6 Application Life

The application life of Type I or Type II adhesive shall be determined by mixing the adhesive components in a 200 ml beaker (5 in. tall x 2 - 1/4 in. diameter).[†] One hundred fifty grams of epoxy resin or epoxy resin blend, shall first be weighed out in the beaker. Nine grams of curing agent shall be added and viscosity measurements shall be made using a Brookfield LVF viscometer with a #4 spindle at 6 rpm (or an equivalent combination which will measure up to 160,000 cps). The time to reach 160,000 cps shall be noted to establish conformance to 4.4.3.1.1.

5.3.6.7 Lap Shear Strength - (Type I and Type II)

5.3.6.7.1 Test Specimens

The lap shear specimen shall consist of 2024-T3 (QQ-A-250/5) alclad aluminum panels, 1 by 4 by 0.063 inches (25 x 100 x 1.6 millimeters (mm)).

5.3.6.7.2 Surface Preparation

Prior to bonding or applying adhesive to test specimens, the surfaces shall be prepared as follows:

The aluminum specimens shall be wiped clean with methyl ethyl ketone (MEK) followed by an immersion for 10 to 12

minutes at 150° to 160°F (66° to 71°C) (339° to 344°K) in a solution containing 30 parts by weight deionized water, 10 parts by weight commercial grade sulfuric acid and 1 to 2 parts by weight commercial grade sodium dichromate. Specimens shall then be rinsed with deionized water and allowed to air dry or oven dry below 150°F (66°C) (339°K) for 30 minutes minimum.

5.3.6.7.3 Adhesive Application

A uniform coat of adhesive, approximately 0.002 to 0.003 inch (50 to 75 micrometers (μm)) thick, shall be applied to both faying surfaces of the test specimens.

5.3.6.7.4 Assembly and Cure

The test specimens shall be placed in an appropriate holding fixture to maintain a 13 mm (0.5 inch) overlap. Using vacuum bag or spring, apply approximately 12 psi (82.7 kilopascals) pressure to the specimens. The assembly shall then be placed in a preheated circulating air oven, heated to 115 ± 8°C (230° ± 15°F). The test assembly shall be maintained at 115 ± 8°C (230° ± 15°F) for 8 hours ± 10 minutes. The assembly shall be cooled to room temperature, and after vacuum bag or clamps are removed, inspected to assure that a continuous adhesive band has been formed around the joint.

5.3.6.7.5 Testing

The lap shear strength shall be determined in accordance with ASTM D1002. The average of four specimens shall be in conformance with 4.4.3.2.

5.3.6.8 Peel Strength

5.3.6.8.1 Test Specimens

T-peel test specimens shall be prepared in accordance with ASTM D1876 using a polyimide-glass fabric laminate adherend* and 0.025 mm (0.001 inch) thick polyphenylethersulfone film for Type I specimens and 0.025 mm (0.001 inch) polyvinyl fluoride (Tedlar) for Type II specimens. Five specimens shall be prepared for each type of adhesive.

*MIL-G-9084 Type VIII fabric impregnated with Kerimid 601, or equivalent polyimide resin.

5.3.6.8.2 Surface Preparation

The polyimide-glass laminate and the film bonding surfaces shall be scrubbed with an institutional cleaner such as Ajax or similar material, and rinsed with tap and deionized water.

5.3.6.8.3 Adhesive Application

Both adherends shall be adhesive coated in accordance with 5.3.6.7.3.

5.3.6.8.4 Assembly and Cure

The peel specimens shall be assembled and cured in accordance with 5.3.6.7.4.

5.3.6.8.5 Testing

The T-peel strength shall be determined in accordance with ASTM D-1876 for conformance to 4.4.3.2.

5.3.6.9 Transparency

The transparency shall be determined by casting Type I or Type II adhesive (0.050-0.125 mm thick) (2 - 5 mils thick) on clear plastic or glass, and then placing the cured specimen over newsprint.

5.3.6.10 Flammability

Flammability properties of Type I or Type II adhesives shall be determined in accordance with ASTM D568, except that samples shall be 25 mm wide by 100 mm long (1 in. wide by 4 in. long).

Table III. Qualification Tests

Examination or Test	Requirement	Test Method
Epoxide Equivalent Weight	Table I	5.3.6.1
Viscosity, Brookfield	Table I	5.3.6.2
Color, Gardner, Maximum	Table I	5.3.6.3
Specific Gravity	Table I	5.3.6.4
Phosphorus Content	Table I	5.3.6.5
Application Life	4.4.3.1.1	5.3.6.6
Lap Shear Strength	Table II	5.3.6.7
Peel Strength	Table II	5.3.6.8
Transparency	4.4.3.3	5.3.6.9
Flammability	4.4.3.4	5.3.6.10

Table IV. Test Specimens

Test	Sample Size	No. of Specimens	Requirement	Test Method
Epoxide Equivalent	(0.001-0.002 gm eq)	1	Table I	5.3.6.1
Viscosity	500 ml. (dil. soln)	1	Table I	5.3.6.2
Color, Gardner	10 - 15 ml.	1	Table I	5.3.6.3
Specific Gravity			Table I	5.3.6.4
Phosphorus Content (epoxy)			Table I	5.3.6.5
Application Life	25 x 100 x 6 mm	1	4.4.3.1.1	5.3.6.6
Lap Shear Strength	25 x 100 x 1.5 mm	8	Table III	5.3.6.9
Peel Strength	305 x 152 x 6 mm			
	305 x 152 x 0.125 mm	8	Table III	5.3.6.10
Transparency	75 x 75 x 0.125 mm	1	4.3.2.3	5.3.6.11
Flammability	25 x 100 x 0.125 mm	3	4.3.2.4	5.3.6.12